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TITLE: SO_2 and H_2S Removal by $CaCO_3$-Based Sorbents at High Pressures

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I. ABSTRACT

OBJECTIVE: The theoretical and experimental investigation of the mechanism of SO_2 and H_2S removal by $CaCO_3$-based sorbents (limestones and dolomites) in pressurized fluidized-bed coal combustors (PFBC) and high pressure gasifiers, respectively, is the main objective of this study. Reactivity evolution experiments will be carried out using thermogravimetry and fluidized-bed reactor (high pressure) arrangements. The pore structure of fresh, heat-treated, and half-calcined solids (dolomites) will be analyzed using a variety of methods. Our work will focus on limestones and dolomites whose reaction with SO_2 or H_2S under atmospheric conditions has been studied by us or other research groups in past studies. Several theoretical tools will be employed to analyze the obtained experimental data including a variable diffusivity shrinking-core model and models for diffusion, reaction, and structure evolution in chemically reacting porous solids.

WORK DONE AND CONCLUSIONS: The development of a thermogravimetric analysis system for gas-solid reaction studies at high pressures was completed. The system was used to obtain some preliminary results on the reactions of limestones with H_2S and SO_2 at high pressures under calcining or noncalcining conditions. The results were in good agreement with the behavior expected on the basis of past studies conducted at atmospheric pressure. Accidental leaks of oxygen into the N_2-H_2S stream that was employed for sulfidation studies suggested that with small amounts of oxygen present in the feed, the behavior of the limestones could be completely different from that observed with oxygen-free feed. Sulfidation experiments were thus carried out in the presence of known quantities of oxygen in the feed using limestones or precalcined samples. The results showed that the concentration of oxygen in the feed has a very strong effect on the behavior of the weight change (uptake of sulfur) during the process. For uncalcined samples, the weight goes through a maximum (probably because of the occurrence of the CaS-$CaSO_4$ reaction) for low values of oxygen concentration in the feed (lower than about 0.3% for 7,000 ppm H_2S in the feed), decreasing for large reaction times to levels that may not be much higher than the initial weight, whereas for higher O_2 concentrations, there is no maximum in the weight evolution curve, and it is possible to observe weights that correspond to complete conversion of CaO to $CaSO_4$. Mathematical models developed in past studies and at the earlier stages of this project were used to

analyze the sulfidation and sulfation data that were obtained from the experiments.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM: Successive conclusion of this research project will provide those working in the area of sulfur dioxide emissions control from PFBC reactors or H2S removal in high pressure gasification systems with fundamental information needed for improving sorbent utilization in such units. It will also generate several new results on the fundamental processes involved in gas-solid reactions occurring in porous media, which may find use in the study of many gas-solid reactions encountered in the area of fossil energy conversion and utilization.

PLANS FOR THE COMING YEAR: For the remaining part of the performance period of the project, our efforts will primarily be focused on the completion of the experimental investigation of the reactions of limestones with SO_2 and H_2S at high pressure under calcining or noncalcining conditions and the analysis of the experimental data using the mathematical models developed in past studies for reaction under atmospheric or simulated high pressure conditions.

II. HIGHLIGHT ACCOMPLISHMENTS

The development and construction of a high-pressure thermogravimetric analysis system was completed, and the system was used to obtain some preliminary results on the reactions of limestones with SO_2 and H_2S.

Experiments on the successive and simultaneous calcination and sulfidation of limestones were carried out in the presence of small concentrations of oxygen in the feed.

III. ARTICLES AND PRESENTATIONS

Sotirchos, S.V., Dhungana, B., Comparative Study of the Sulfation and Sulfidation Reactions of Limestones Undergoing Simultaneous Calcination, 1997 Annual AIChE Meeting, Los Angeles, CA, November 1997.

Sotirchos S.V., Computation of Transport Properties of Multiphase, Anisotropic Media Using Random Walk Schemes on 3-Dimensional Pixelized Images, to be presented at the 9th Int. Conf. on Modern Materials and Technologies, Florence, Italy, June 1998.

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STUDENTS THAT HAVE BEEN SUPPORTED BY THIS GRANT SINCE ITS INCEPTION:

P. Aghalayam, M.S., S. Serbezov, Ph.D., B. Dhungana, M.S.

PUBLICATIONS AND PRESENTATIONS SINCE THE INCEPTION OF THE GRANT:

Sotirchos, S.V., Transvalidou, F., Stochastic Simulation Algorithms for the Computation of the Transport Properties of General Anisotropic Composite or Porous Media, 1996 ACerS Annual Meeting, Indianapolis, April 1996.

Sotirchos, S.V., Performance Analysis of CaO-Based Sorbents during in Situ Desulfurization of Fuel Gas, NATO Advanced Study Institute on Desulfurization of Coal Gas with Regenerable Metal Oxide Sorbents, Izmir, Turkey, July 1996.

Sotirchos, S.V., Modelling of H_2S Removal from Coal Gas Using Bulk Sorbents, NATO Advanced Study Institute on Desulfurization of Coal Gas with Regenerable Metal Oxide Sorbents, Izmir, Turkey, July 1996.

Sotirchos, S.V., Modelling of H_2S Removal from Coal Gas Using Supported Sorbents, NATO Advanced Study Institute on Desulfurization of Coal Gas with Regenerable Metal Oxide Sorbents, Izmir, Turkey, July 1996.

Sotirchos, S.V., Dhungana, B., Comparative Study of the Sulfation and Sulfidation Reactions of Limestones Undergoing Simultaneous Calcination, 1997 Annual AIChE Meeting, Los Angeles, CA, November 1997.

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